

PCT

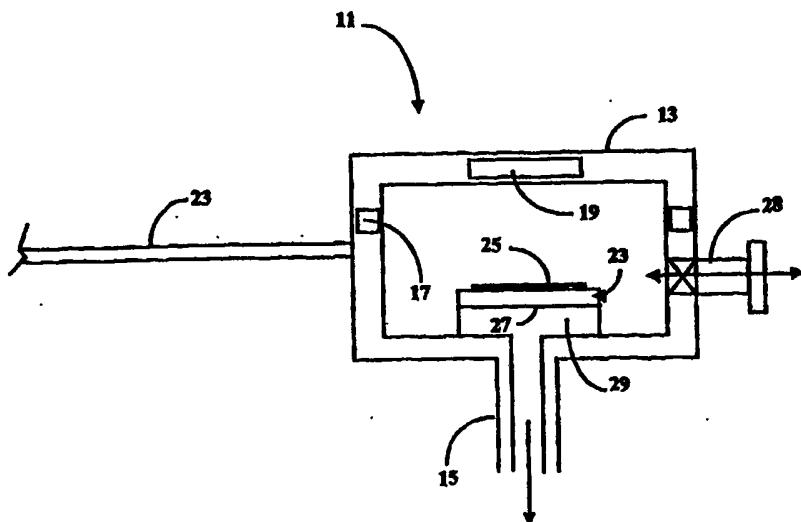
WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B05D 5/12, C23C 16/34, H05H 1/24, B32B 18/00, G11B 5/66		A1	(11) International Publication Number: WO 98/23389 (43) International Publication Date: 4 June 1998 (04.06.98)
(21) International Application Number: PCT/US97/21449		(81) Designated States: JP, KR, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(22) International Filing Date: 24 November 1997 (24.11.97)		Published <i>With international search report.</i>	
(30) Priority Data: 08/756,562 26 November 1996 (26.11.96) US			
(71) Applicant: GENUS, INC. [US/US]; 1139 Karlstad Drive, Sunnyvale, CA 94089 (US).			
(72) Inventors: GADGIL, Prasad, N.; 3840 Granada Avenue #236, Santa Clara, CA 95051 (US). GALEWSKY, Carl, J.; 170 Aromitas Road, Aromas, CA 95004 (US).			
(74) Agent: BOYS, Donald, R.; P.O. Box 187, Aromas, CA 95004 (US).			

(54) Title: NITROGEN-BEARING CVD FILMS FROM NF₃, AS A NITROGEN SOURCE



(57) Abstract

Processes for forming nitride films in integrated circuit manufacture are accomplished by chemical vapor deposition using nitrogen fluoride (NF₃) as a nitrogen-bearing gas providing nitrogen to the nitride film. The method includes the steps of placing a substrate in a CVD reactor chamber (11), heating the substrate (25), and flowing the precursors including nitrogen fluoride over the surface of the heated substrate to form the nitride films. Process examples are provided wherein the nitrided films are tungsten nitride, tungsten silicon nitride, and titanium silicon nitride. Process variations include film formation with and without plasma enhancement, and provision of silicon to films be either silane or disilane.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SR	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

Nitrogen-Bearing CVD Films From NF₃ as a Nitrogen Source

*By Inventors
Prasad Gadgil and Carl Galewski*

5

Field of the Invention

The present invention is in the area of methods and apparatus for processing wafers as a step in manufacturing integrated circuits (ICs), 10 and relates in particular to chemical vapor deposition (CVD) and plasma-enhanced chemical vapor deposition (PECVD) of tungsten or titanium with silicon and nitrogen, using NF₃ as a gaseous source of nitrogen in the processes.

15

Background of the Invention

Manufacturing of integrated circuits is historically a procedure of forming thin films and layers of various materials on wafers of base semiconductor material, and then selectively removing areas of the films 20 to produce structures and circuitry. Doped silicon is a typical base wafer material, and in various process schemes, metal layers are formed on the doped silicon or on polysilicon or silicon oxide formed from the base material. It is well-known in the art that there are many difficulties in forming thin metal films, and in particular in forming such films on 25 non-metallic base materials. Among these difficulties are problems of adhesion, and problems related to diffusion and reaction of materials across material boundaries.

There are a number of well-developed technologies for deposition of materials in the ultra-thin layers required for IC fabrication 30 schemes. The deposition techniques can be roughly classed as either physical vapor deposition (PVD) or Chemical Vapor Deposition (CVD)

- 2 -

techniques. PVD processes include such processes as evaporation and re-condensation, wherein a material, typically a metal, is heated to a temperature at which the metal melts and vaporizes. The metal then condenses on surfaces generally in line-of-sight of the evaporation,

5 forming a film.

Another PVD process is the well-known sputtering process, wherein a plasma of usually an inert gas is formed near a target material, and the target is biased to attract ions from the plasma to bombard the target. Atoms of the target material are dislodged by momentum

10 transfer, and form an atomic flux of particles which coalesce on surrounding surfaces generally in line-of-sight of the target surface eroded by the sputtering process.

PVD processes have distinct advantages for some processes, such as high rate of deposition, and relatively simple coating apparatus.

15 There are drawbacks as well, notably an inherent inability to provide adequate step coverage. That is, on surfaces having concavities as a result of previous coating and etching steps, PVD processes are prone to shadowing effects resulting in local nonuniformity of coating thickness. This problem has grown in importance as device density has increased

20 and device geometry has shrunk in size. with multi-level interconnect schemes involving vias and trenches on microscopic scale.

CVD processes comprise deposition from gases injected into a chamber, wherein the gases or components of the gases are chemically decomposed and/or recombined by energy input. In typical CVD

25 processes the substrate to be coated is heated, and gases introduced into a chamber holding the substrate react at or very near the substrate surface in a manner to deposit a film of material on the surface. For example, a film of metallic tungsten may be deposited on a heated substrate surface by flowing Tungsten hexafluoride to the surface in

30 conjunction with a reducing gas, such a hydrogen. Resulting chemical

reaction at a hot substrate surface reduces the tungsten hexafluoride, depositing a film of tungsten on the substrate, and producing HF gas.

It is well-known in the art that there are a wide variety of CVD processes known and available for semiconductor circuit processes,

5 including deposition from organo-metallic materials and plasma-enhanced CVD, wherein energy is added to the process by exciting the gas above the deposition surface with a high-frequency discharge (plasma).

In the fabrication of an integrated circuit, transistors are
10 developed on the surface of a doped silicon substrate. Once transistors are formed, to make a circuit, gates and drains have to be interconnected with electrically conductive tracks. This point in the overall IC fabrication process serves as perhaps the best example of a thin-film interface between a substrate material and an electrically-conductive
15 metal.

Over several years in the IC industry, a variety of materials have been tested for interconnecting tracks. Among these are aluminum, titanium, tungsten, and gold. Each has advantages and drawbacks, and different characteristics related to interaction with silicon, electrical
20 conductivity, and electromigration, among others. Also, specific deposition processes have been developed suitable for specific materials.

Aluminum, for example is typically deposited by the PVD process of sputtering, and there is currently no commercialized process for CVD deposition of aluminum as an interconnect material. Tungsten, on the
25 other hand, can be conveniently deposited by a CVD process.

There are a variety of known CVD processes employing variations of known chemistries to produce a variety of films of a single element, or a combination of two or more elements. Tungsten is deposited as a continuous (blanket) film on substrates, for example, to
30 provide, after etching, both via plugs and interconnect tracks between

- 4 -

devices implemented in doped silicon. Combinations of tungsten with other elementss are deposited for other purposes, such as adhesion and barrier layers on gates of transistors implemented in silicon as an intermediate layer to improve adhesion and combat diffusion, for 5 example, of silicon from the gates into the interconnect film. In these applications the films deposited directly on the gates prior to the interconnect material are called barrier layers.

One of the elements frequently combined with tungsten to provide specific desirable characteristics of a resulting film for adhesion 10 and barrier purposes is Nitrogen to form tungsten nitride. The inventors are aware of conventional chemistry and processes for deposition of WN_x (Tungsten Nitride). In some instances it is desirable to combine tungsten with other elements as well as Nitrogen. One such combination of interest and potential use in gate technology is Tungsten-15 Silicon-Nitride.

There are also elements competitive to tungsten for gate processes. One of these is Titanium, and materials of interest in combination with Titanium are Titanium Nitride(TiN) and Titanium Silicon Nitride ($Ti_xSi_yN_z$).

20 The common element among the materials described above is Nitrogen, and perhaps the most common gas utilized as a source of Nitrogen in the CVD processes is ammonia (NH_3). It is well known in the art that there are many problems with handling NH_3 and mixing NH_3 with other gaseous components for CVD processes. One such 25 component is WF_6 which, when combined with NH_3 at room temperature produces an instantaneous and highly exothermic chemical reaction. Such a gas phase reaction is highly undesirable because it leads to serious complications in CVD reactor design and operation. Also an undesirable gas phase reaction leads to particulate formation, 30 powdery deposits, and poor adhesion of films to the substrate. In

- 5 -

addition to this, the instantaneous reaction between WF₆ and NH₃ leads to coating on the reactor (process chamber) walls. This coating contributes significantly to particles due to peeling, and hence reactors must be completely and periodically cleaned for operation in the actual
5 production environment.

For these and other reasons it is desirable to develop and demonstrate alternative chemistries for the deposition of transition metal nitrides and silicon nitrides.

10 Summary of the Invention

In a preferred embodiment of the present invention a method is provided for forming a nitrided film of a transitional metal on a surface of a substrate. The method comprises steps of (a) placing the substrate
15 in a reactor chamber; (b) heating the substrate; and (c) flowing a gas bearing the transitional metal, nitrogen trifluoride (NF₃), and hydrogen (H₂) into the reactor chamber and over the surface of the heated substrate.

The gas bearing a transitional metal in some embodiments is
20 tungsten hexafluoride (WF₆). In other embodiments the gas bearing a transitional metal is titanium tetrachloride (TiCl₄).

In one of the preferred embodiments wherein the gas bearing a transitional metal is WF₆, a tungsten nitride (WN_x) film on a surface of a substrate is formed in a process comprising steps of (a) placing the
25 substrate in a reactor chamber; (b) heating the substrate; and (c) flowing tungsten hexafluoride (WF₆), nitrogen trifluoride (NF₃), and hydrogen (H₂) into the reactor chamber and over the surface of the heated substrate. In another of the preferred embodiments wherein the gas bearing a transitional metal is WF₆, a tungsten nitride (WN_x) film is

- 6 -

formed in a process comprising steps of (a) placing the substrate in a reactor chamber; (b) heating the substrate; (c) flowing tungsten hexafluoride (WF_6), nitrogen trifluoride (NF_3), hydrogen (H_2), and an inert gas into the reactor chamber; and (d) striking a plasma over the substrate. In this and other plasma enhanced processes according to varying practices of the present invention, the substrate temperature is typically lower than for those processes within the scope of the invention wherein a plasma is not used. Various inert gases may be used in the plasma enhanced processes according to 5 embodiments of the present invention, but argon is preferred.

10

In some preferred embodiments a silicon-bearing gas is separately introduced along with WF_6 , and a tungsten silicon nitride ($W_xSi_yN_z$) film is formed. These films are formed in various 15 embodiments both with and without plasma enhancement as well. The silicon-bearing gas in some embodiments is silane (SiH_4), and in others the silicon-bearing gas is disilane (Si_2H_6).

In a class of unique processes according to an embodiment of the invention, titanium silicon nitride ($Ti_xSi_yN_z$) films are formed on a surface of a substrate. These processes comprise steps of (a) placing the 20 substrate in a reactor chamber; (b) heating the substrate; (c) flowing titanium tetrachloride ($TiCl_4$), nitrogen trifluoride (NF_3), a silicon-bearing gas, and hydrogen into the reactor chamber. The processes for forming titanium silicon nitride include processes with and without plasma enhancement. The silicon-bearing gas in some embodiments is 25 silane, and in others is disilane or dichlorosilane. In some embodiments an inert gas is provided in the processing chamber to support a plasma for plasma-enhanced chemical vapor deposition (PECVD).

The processes in embodiments of the invention have particular application for providing contact, adhesion, and barrier films in steps of

integrated circuit manufacturing, wherein the substrate is a silicon wafer having integrated circuit (IC) structures formed thereon.

The processes of the invention are applicable to equipment of many kinds, made by several different manufacturers. In many sorts of 5 such equipment, substrates are moved into processing chambers from a load lock chamber into the reactor chamber. The reactor chamber may be a single-wafer CVD reactor chamber adapted to a cluster tool material handling system, or a batch reactor chamber, wherein, in the step of placing the substrate, a batch of more than one wafer is moved into the 10 CVD reactor chamber from a vacuum load-lock chamber.

The processes described herein as embodiments of the present invention provide many advantages over conventional processes wherein the nitrogen-bearing gas is NH₃, and these advantages have been demonstrated in the laboratory repeatedly. For example, more efficient 15 nitrogen inclusion in the film has been demonstrated, and the results of tests for this parameter are presented below.

Another significant advantage over processes of the prior art is that efficient and complete premixing of gases may be performed, which leads to better film uniformity and to elimination of undesirable gas- 20 phase reaction. Systems according to embodiments of the present invention are therefore simpler to design and construct, and may be used for longer periods of time between cleaning cycles.

Yet another significant advantage for the unique NF₃ chemistry of the present invention as compared to conventional NH₃ chemistry is 25 that the NF₃ chemistry provides significantly better control of film composition. This is so because in the NH₃ chemistry there is competition for WF₆. In the conventional NH₃ chemistry, reaction of WF₆ and NH₃ produces both nitrogen and tungsten, and reaction of WF₆ and H₂ produces tungsten. The dual product of the former reaction 30 results in uncertainty in yield. In the unique NF₃ chemistry of the

- 8 -

present invention there is no such ambiguity. NF_3 reacting with H_2 produces nitrogen, and reaction of WF_6 and H_2 produces tungsten. This parallel co-reduction provides for straightforward control of film composition not available in the conventional NH_3 chemistry.

5

Brief Description of the Drawing Figures

Fig. 1 is a cross-section elevation view of a single wafer CVD deposition reactor for practicing the present invention.

Fig. 2 is a process diagram for deposition of WN_x in an embodiment of the present invention, without plasma enhancement.

Fig. 3 is a process diagram for deposition of WN_x in an embodiment of the present invention, with plasma enhancement.

Fig. 4 is a process diagram for deposition of $\text{W}_x\text{Si}_y\text{N}_z$ in an embodiment of the present invention.

Fig. 5 is an alternative process diagram for deposition of $\text{W}_x\text{Si}_y\text{N}_z$ in an embodiment of the present invention.

Fig. 6 is a process diagram for deposition of $\text{Ti}_x\text{Si}_y\text{N}_z$ in an embodiment of the present invention.

Fig. 7 is a process diagram for deposition of $\text{Ti}_x\text{Si}_y\text{N}_z$ an alternative embodiment of the invention.

Fig. 8 is a graph of film content for tungsten nitride films made with NF_3 chemistry according to an embodiment of the present invention, and with conventional NH_3 chemistry.

30

Description of the Preferred Embodiments

Fig. 1 is a simplified cross-section elevation view of a single wafer CVD reactor chamber 11 for practicing the present invention.

5 Single wafer chambers are highly desirable in current art for adaptation to processing systems known generally as cluster tools, wherein one wafer at a time may be moved through vacuum load locks and sequentially through a number of individual processes before again being exposed to air. Pick-and-place transfers, not shown in Fig. 1,

10 operating in a transport volume maintained at a high vacuum level, move wafers from one chamber to another for processing, and the individual processing chambers are isolated from the transport volume during processing. In Fig. 1 transfer of wafers is made through valved port 28. A number of such machines are known to the inventors, and

15 among them is the Genus Series 7000TM machines, made by Genus, Inc. of Sunnyvale, CA.

In the reactor of Fig. 1 a hermetically sealed chamber 13 is pumped through a pumping port 15 by a vacuum pumping system not shown, and gaseous process material are introduced via a ring manifold arrangement 17 and a showerhead manifold arrangement 19 from a remote gas supply system through manifolding 23. The showerhead is typically electrically isolated from other metallic portions of the chamber, and may be grounded or connected to high-frequency power supplies for electrical biasing. A gas mixing manifold (not shown) in this arrangement ensures that gases introduced into the showerhead manifold are thoroughly mixed.

Susceptor 23 is the CVD hearth in this embodiment, and supports a wafer 25 for processing. The hearth, and hence the wafer, is heated by a plate heater 27 within an enclosure volume 29, and

30 arrangements provide for an ability to flow gases into this volume and

- 10 -

onto the backside of a wafer during processing. Susceptor 23 is also electrically isolated and may be either grounded or biased as desired, such as by a high frequency power supply not shown. Various sensors for measuring process parameters such as temperature and pressure are 5 also interfaced with the CVD reactor, although not specifically shown in Fig. 1. It will be apparent to those with skill in the art that the features mentioned here but not shown are well-known in the art.

CVD reactor 11 depicted in Fig. 1 is well-suited for conducting CVD processes according to the present invention. It will be apparent 10 to those with skill in the art, however, that the invention is not limited to the reactor shown, and may be practiced in a wide variety of CVD reactors, including those reactors known as batch reactors in the art, wherein several wafers at a time are transferred into a reactor chamber, and processed in the reactor simultaneously.

15

Chemistry for Deposition of Tungsten Nitride - WN_x

In current art WF₆ with NH₃ is the most common chemistry, and the only commercially developed chemistry for the deposition of 20 Tungsten Nitride thin films by CVD or PECVD. There is, however, a serious drawback to this chemistry. That is, as described above, the fact that mixing these two gases at room temperature causes an instantaneous and highly exothermic reaction. This fact leads to considerable complications in CVD reactor design and operation. The undesirable 25 gas phase reactions, even where the gases are not premixed, causes particulate formation, powdery deposits, coating of chamber walls, and to poor film adhesion to the substrate.

The inventors have developed Tungsten Nitride processes using NF₃ as a nitrogen source, providing significant simplification in process 30 chemistry as well as in reactor design and operation. In light of

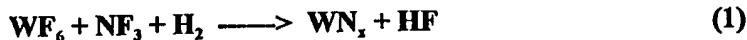
- 11 -

reactivity of WF_6 and NH_3 , these substances must be injected separately and also very evenly over a heated substrate surface to achieve uniform film deposition. In addition, to minimize the undesirable gas phase reaction, these gases must be so injected that they react just above the
5 substrate surface. Such constraints lead to complications in the design of the gas distribution manifold, the shower-head and in reactor operation. Such complications invariably affect the large area film uniformity adversely.

The inventors have found that employing NF_3 in lieu of NH_3
10 removes these constraints completely. Since NF_3 and WF_6 do not react with each other or with H_2 at room temperature, they can be thoroughly mixed prior to injection, and the resultant mixture can be evenly distributed over the entire deposition surface with simplicity and efficiency. The use of NF_3 thus simplifies the CVD reactor design and
15 its operation. The premature and undesirable gas phase reactions and wall coatings are also minimized.

New and unique CVD process for tungsten nitride films in an embodiment of the present invention is expressed in a general chemical formula as:

20



This chemistry is effective for depositing tungsten nitride without plasma enhancement and also with plasma enhancement
25 (PECVD). Fig. 2 is a process diagram for an exemplary CVD process using NF_3 without plasma enhancement for producing WN_x and Fig. 3 is a diagram for a for an exemplary process for deposition of WN_x with use of plasma enhancement.

There are, in Fig. 2 and other exemplary process diagrams below,
30 separate charts depicting important variables in the processes. For

example, in Fig. 2, total chamber pressure is shown in upper chart 31, wafer temperature is shown in middle chart 33, and process gas flows are shown in bottom chart 35. Time is shown in all charts on the horizontal scale.

5 It will be apparent to those with skill in the art that there will be deviations that may be made without departing from the spirit and scope of the invention. For example, more or less time could be taken and other variables adjusted to suit, and there are ranges within which pressures and gas flows will still be effective to produce films of
10 desirable composition. As described above, the charts shown are exemplary.

In Fig. 3 the tungsten nitride process is shown with the unique chemistry, but with energy added by virtue of plasma enhancement. Plasma power is shown in the middle chart of Fig. 3 along with substrate
15 temperature. Plasma power is provided in the process depicted by Fig. 3 at about the seventy-second mark at a level of 125 Watts, and is continued to about 290 seconds. It will be apparent to those with skill in the art that the time duration for deposition depends on the thickness of film desired. The substrate temperature for the PECVD process of Fig.
20 3 is about 350 degrees C., while for the process depicted in Fig. 2, without plasma enhancement, the substrate temperature is about 500 degrees C.

Hydrogen is a common reducer (reducing agent) for WF_6 and NF_3 . Both of these chemicals neither react with each other nor with
25 hydrogen upon mixing at room temperature. Hence, these gases can be, and in preferred embodiments of the present invention are, mixed together before they are brought into the process volume to be passed over the substrate.

NF_3 , with a boiling point of -129 C is a stable gas, which becomes
30 reactive upon heating above 250-300 C. (See F. A. Cotton and G.

Wilkinson, in "Advanced Inorganic Chemistry", 3rd ed., p.363, Wiley and Co., New York, 1972).

Increased reactivity of NF₃ at temperatures > 250 C as compared to NH₃ is believed by the inventors to be useful in lowering the deposition temperature for CVD WN_x films and increasing efficiency of inclusion of Nitrogen into developing films. Increased inclusion efficiency is discussed further below with the aid of Fig. 8.

The CVD process without plasma enhancement is particularly preferred because this process exhibits a higher degree of step coverage than does the plasma enhanced process

In PECVD development using the above NF₃ chemistry for depositing WN_x films, results show that amorphous WN_x films can be deposited with the above-described chemistry between 300 - 370 C at 100 mTorr total process pressure. The ratio NF₃ / WF₆ has been varied in these experiments from 0.5 to 3.0 with the flow of WF₆ varied between 5 and 10 sccm (standard cubic centimeters per minute). Hydrogen was added in excess of 400 sccm to this mixture.

It is known that a mixture of NF₃ and H₂ is explosive in the range of 5 mol % to 90 mol % of H₂ [See either J. G. Langan, "Flammability Test Results of NF₃, H₂ and SiH₄ Mixtures", in internal memorandum, "Air Products and Chemicals", Allentown, PA. March 20, 1995; or US Patent No. 3,235,474. Assignee : Air Products Inc).

The gaseous mixture introduced in the reaction chamber with the composition as described above is within the range of non-explosivity. In addition to this, the explosivity experiments from the reference above were performed at atmospheric pressure. The chamber pressure in the process embodiment described is, however, 100 mTorr. The explosive nature of reaction of NF₃ with H₂ may be one of the reasons for efficiency of incorporation of N in WN_x film in processes incorporating NF₃ as the Nitrogen source. In addition, a temperature range of from

300 - 450 C for the process has been established, and a pressure range of from 50 mTorr to 2 Torr.

Chemistry for Deposition of $W_xSi_yN_z$

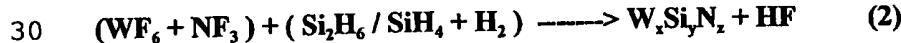
5

Films with composition $W_xSi_yN_z$ ($x = 0.45 - 0.47$, $y = 0.08 - 0.1$ and $z = 0.44 - 0.46$) have been shown to be excellent diffusion barriers for Cu, mainly due to an ability of Si atoms to prevent formation of crystalline phase (See Paul M. Smith et al., Proc. 1996 VIMC

10 Conference, p. 162, June 18-20, 1996, Santa Clara). In the experiments covered in this reference $W_xSi_yN_z$ films were deposited by employing WF_6 , NH_3 and disilane Si_2H_6 , chemistry at 350 C and at 500 - 700 mTorr.

15 These films could not be grown by silane (SiH_4) chemistry at this temperature because of higher thermal stability of the SiH_4 molecule compared to Si_2H_6 . It has been postulated that NH_3 adsorbs strongly on the surface of the growing film and thereby reduces the sticking coefficient of WF_6 and Si_2H_6 thus lowering the deposition rate.

20 In this context, replacement of NH_3 by NF_3 in the deposition chemistry to deposit $W_xSi_yN_z$ films by CVD is advantageous. The extent of adsorption of NF_3 molecule on the growing film is less compared to NH_3 molecule due to highly polar and electronegative character of Fluorine in the N-F bond. This fact increases film deposition rate with other factors held constant. Also, the reactivity of NF_3 with SiH_4 helps 25 destabilize the silane molecule and thereby accomplishing deposition with silane at lower temperatures than is possible with the corresponding NH_3 process. The overall reaction in the unique NF_3 process, using either silane or disilane, is:



Here, silane/disilane and hydrogen are common reducers for WF_6 and NF_3 . Thus, the advantages of NF_3 as a Nitrogen source are (a) increased deposition rate (b) use of silane in place of disilane (c) lower deposition temperature compared to the NH_3 process, and (d) better control of stoichiometry by parallel co-reduction chemistry.

In the two-component mixture of SiH_4 and NF_3 , the concentration of SiH_4 greater than 0.66 mol% and less than 95.3% is explosive. Thus, the gaseous mixture of WF_6 , NF_3 , and SiH_4 are considerably diluted with hydrogen in order to operate the process safely. It is also necessary to separate the reactants as shown with parenthesis in the above equation before they reach the wafer surface because silane and disilane both react with WF_6 and NF_3 instantaneously at room temperature. Some appropriate ranges of conditions for deposition are: wafer temperature : 300 C - 500 C.; system pressure : 50 mTorr to 10 Torr.; H_2 flow rate > 500 sccm.; WF_6 flow rate varied from 4 sccm to 10 sccm.; $0.625 < (\text{NF}_3 / \text{WF}_6) < 3.5$ and $0.5 < (\text{SiH}_4 / \text{NF}_3) < 5.0$.

Fig. 4 is a process diagram for deposition of $\text{W}_x\text{Si}_y\text{N}_z$ using silane and NF_3 , and Fig. 5 is a process flow diagram for deposition of $\text{W}_x\text{Si}_y\text{N}_z$ using disilane and NF_3 . The chemical process as described in equation 2 can be performed in plasma enhanced CVD mode as well, much as described above for tungsten nitride films.

25

Chemistry for deposition of $\text{Ti}_x\text{Si}_y\text{N}_z$

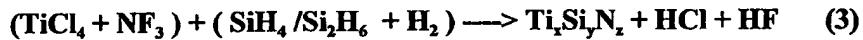
Thin films with composition $\text{Ti}_{0.46}\text{Si}_{0.03}\text{N}_{0.51}$ have been deposited in the prior art by employing $\text{Ti}[\text{N}(\text{C}_2\text{H}_5)_4]$ tetrakis-dethylamido titanium, (TDEAT) as a titanium source and SiH_4 and NH_3 as Si and

- 16 -

Nitrogen sources respectively in the temperature range of 300 - 450 C at 20 Torr. TDEAT is an expensive organometallic source material and also reacts with both SiH₄ and NH₃ upon mixing, and hence the flow of TDEAT must be separated from these two precursors in the manifold.

5 Silane doesn't thermally react with ammonia in the temperature range of deposition and thus the Si content of the film can be varied by either increasing the silane content in the flow or by increasing the deposition temperature. However, by employing NF₃ in lieu of NH₃, which reacts spontaneously with silane or disilane, one can vary the Si content in the
10 film and better control its barrier properties. The parallel co-reduction chemistry described above unique to the NF₃ chemistry of the present invention is an added benefit.

The general reaction for Ti_xSi_yN_z films in embodiments of this
15 invention is:



Thin films of Ti_xSi_yN_z are deposited in an embodiment of the
20 present invention by employing a simple and inexpensive TiCl₄ chemistry in conjunction with either silane or disilane. The precursors must be separated as shown in equation (3) above to avoid undesirable vapor phase pre-reaction. The range of conditions for deposition are : wafer temperature : 300 C - 600 C., system pressure : 50 mTorr to 20
25 Torr. H₂ flow rate from 300 to 500 sccm. TiCl₄ flow rate varied from 5 sccm to 20 sccm. 0.625 < (NF₃ / TiCl₄) < 3.5 and 0.5 < (SiH₄ / NF₃) < 5.0 .

Fig. 6 is a process diagram for an exemplary process for deposition of Ti_xSi_yN_z in an embodiment of the present invention, using
30 silane. Fig. 7 is a process diagram for an exemplary process for

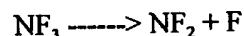
deposition of $Ti_xSi_yN_z$ in an embodiment of the present invention, using disilane. The process described in equation 3 may be performed also in Plasma Enhanced CVD mode, much as described for the other exemplary processes described above.

5

Summary

In all the process chemistries described in equations (1) - (3), the by-product HF is evolved in large quantities. HF reacts with materials 10 such as silica and BPSG (Boro-Phospho-Silicate Glass) commonly used in microelectronic device fabrication. To suppress such undesirable side reaction, it is desirable to saturate the deposition surface with NH_3 , SiH_4 , or Si_2H_6 in-situ, before the initiation of deposition. Such a process modification prevents potentially detrimental effects of NF_3 chemistry 15 on interface quality.

Further to this, the plasma enhanced CVD processes described above involving NF_3 are modified by an addition of an inert gas such as Helium or Argon. It is well known that a deposition plasma consists of highly energetic free electrons which are necessary to sustain a plasma. 20 In NF_3 , the highly electronegative character of F tends to extract electrons from the plasma and make it unstable. Such plasma instabilities in turn tend to adversely affect the PECVD process repeatability and also film uniformity. Addition of an inert gas such as He or Ar (preferably Ar) supplies electrons by ionization in the plasma. 25 The mechanism is described below :



It will be understood by those with skill in the art that the addition of inert gas into the chamber to support a plasma for PECVD processing is well-known in the art.

A significant advantage of NF₃ chemistry in all of its forms in the 5 present disclosure is the co-reduction characteristic as described above. Because each of the desired products of the composite films is formed in an essentially independent chemical reaction, control of film composition is straightforward and predictable.

The inventors have also have discovered, as an added advantage 10 in the NF₃ processes described, that NF₃ chemistry is more efficient than NH₃ chemistry for providing nitrogen in the desired film. Fig. 8 is a graph prepared from experimental data collected in practicing the tungsten nitride NF₃ processes described above and in practicing conventional tungsten nitride NH₃ processes. As is well known in the 15 art from the conventional processes, the films prepared are a mixture of tungsten and tungsten nitride (W₂N) after annealing. The ordinate in the graph represents film content by percent for materials represented in the graph, while the abscissa represents the ratio of nitrogen-bearing gas in the process (either NH₃ or NF₃) to tungsten hexafluoride (WF₆).

20 Curve 35 indicates W₂N percent content for the unique NF₃ process of the present invention, and curve 37 represents W₂N percent for conventional NH₃ processing. It is readily apparent that the W₂N content increases more rapidly for the unique NF₃ process than for the conventional process. For example, a 50% level is reached for NF₃ 25 processing at a ratio of about 0.4, while for conventional NH₃ processing a ratio of about 0.7 is needed for a 50% level.

It will be apparent to those with skill in the art that there are many alternative to the embodiments of the invention as described above without departing from the spirit and scope of the invention. For 30 example, there are a variety of reactors that might be used, including

- 19 -

both single-chamber and batch reactors. There are process variations that may be made as well, including variations in preparatory and finishing steps before and after the principle deposition step in each exemplary process, and there are broad ranges, as have been detailed above, of process characteristics within which successful process has been demonstrated and may be repeated. As there are many such variations within the spirit and scope of the invention, the invention is limited only by the claims which follow:

- 20 -

What is claimed is:

1. A method for forming a tungsten nitride (WN_x) film on a surface of a substrate, comprising steps of:
 - 5 (a) placing the substrate in a reactor chamber;
 - (b) heating the substrate; and
 - (c) flowing tungsten hexafluoride (WF_6), nitrogen trifluoride (NF_3), and hydrogen (H_2) into the reactor chamber and over the surface of the heated substrate.
- 10 2. The method of claim 1 wherein the substrate is a silicon wafer having integrated circuit (IC) structures formed thereon.
- 15 3. The method of claim 1 wherein the step of placing the substrate in a reactor chamber comprises moving the substrate from a vacuum load lock chamber into the reactor chamber.
- 20 4. The method of claim 1 wherein the reactor chamber is a single-wafer CVD reactor chamber adapted to a cluster tool material handling system.
- 25 5. The method of claim 1 wherein the reactor chamber is batch reactor chamber, and in the placing the substrate step, a batch of more than one wafer is moved into the CVD reactor chamber from a vacuum load lock chamber.
6. A method for forming a tungsten nitride (WN_x) film on a surface of a substrate, comprising steps of:
 - (a) placing the substrate in a reactor chamber;
 - (b) heating the substrate;

- 21 -

- (c) flowing tungsten hexafluoride (WF_6), nitrogen trifluoride (NF_3), and hydrogen (H_2) into the reactor chamber; and
- (d) striking a plasma over the substrate.

5 7. The method of claim 6 wherein the substrate is a silicon wafer having integrated circuit (IC) structures formed thereon.

8. The method of claim 6 wherein the step of placing the substrate in a reactor chamber comprises moving the substrate from a vacuum load

10 lock chamber into the reactor chamber.

9. The method of claim 6 wherein the reactor chamber is a single-wafer CVD reactor chamber adapted to a cluster tool material handling system.

15 10. The method of claim 6 wherein the reactor chamber is a batch reactor chamber, and in the placing the substrate step, a batch of more than one wafer is moved into the CVD reactor chamber from a vacuum load lock chamber.

20 11. The method of claim 6 further comprising injection of an inert gas.

12. A tungsten nitride (WN_x) film on a surface of a substrate, formed by:

- (a) placing the substrate in a reactor chamber;
- (b) heating the substrate; and
- (c) flowing tungsten hexafluoride (WF_6), nitrogen trifluoride (NF_3), and hydrogen (H_2) into the reactor chamber and over the surface of the heated substrate.

- 22 -

13. A tungsten nitride (WN_x) film on a surface of a substrate, formed by:

- (a) placing the substrate in a reactor chamber;
- (b) heating the substrate;
- 5 (c) flowing tungsten hexafluoride (WF_6), nitrogen trifluoride (NF_3), and hydrogen (H_2) into the reactor chamber and over the surface of the heated substrate; and
- (d) striking a plasma over the substrate.

10 14. A method for forming a tungsten silicon nitride ($W_xSi_yN_z$) film on a surface of a substrate, comprising steps of:

- (a) placing the substrate in a reactor chamber;
- (b) heating the substrate; and
- (c) flowing tungsten hexafluoride (WF_6), nitrogen trifluoride (NF_3), a silicon-bearing gas, and hydrogen into the reactor chamber and over the surface of the heated substrate.

15 15. The method of claim 14 wherein the silicon-bearing gas is silane (SiH_4).

20

16. The method of claim 14 wherein the silicon-bearing gas is disilane (Si_2H_6).

25 17. The method of claim 14 wherein the substrate is a silicon wafer having integrated circuit (IC) structures formed thereon.

18. The method of claim 14 wherein the step of placing the substrate in a reactor chamber comprises moving the substrate from a vacuum load lock chamber into the reactor chamber.

30

- 23 -

19. The method of claim 14 wherein the reactor chamber is a single-wafer CVD reactor chamber adapted to a cluster tool material handling system.
- 5 20. The method of claim 14 wherein the reactor chamber is a batch reactor chamber, and in the placing the substrate step, a batch of more than one wafer is moved into the CVD reactor chamber from a vacuum load lock chamber.
- 10 21. A method for forming a tungsten silicon nitride ($W_xSi_yN_z$) film on a surface of a substrate, comprising steps of:
 - (a) placing the substrate in a reactor chamber;
 - (b) heating the substrate;
 - (c) flowing tungsten hexafluoride (WF_6), nitrogen trifluoride (NF_3), hydrogen, and a silicon-bearing gas into the reactor chamber; and
 - 15 (d) striking a plasma over the substrate.
22. The method of claim 21 wherein the silicon-bearing gas is silane (SiH_4).
- 20 23. The method of claim 21 wherein the silicon -bearing gas is disilane (Si_2H_6).
24. The method of claim 21 further comprising injecting an inert gas into the chamber.
- 25 25. The method of claim 21 wherein the substrate is a silicon wafer having integrated circuit (IC) structures formed thereon.

26. The method of claim 21 wherein the step of placing the substrate in a reactor chamber comprises moving the substrate from a vacuum load lock chamber into the reactor chamber.

5 27. The method of claim 21 wherein the reactor chamber is a single-wafer CVD reactor chamber adapted to a cluster tool material handling system.

10 28. The method of claim 21 wherein the reactor chamber is a batch reactor chamber, and in the placing the substrate step, a batch of more than one wafer is moved into the CVD reactor chamber from a vacuum load lock chamber.

15 29. A tungsten silicon nitride ($W_xSi_yN_z$) film on a surface of a substrate, formed by:

 (a) placing the substrate in a reactor chamber;

 (b) heating the substrate; and

 (c) flowing tungsten hexafluoride (WF_6), nitrogen trifluoride (NF_3), hydrogen, and a silicon-bearing gas into the reactor chamber and 20 over the surface of the heated substrate.

30. The film of claim 29, wherein the silicon-bearing gas is silane (SiH_4).

25 31. The film of claim 29 wherein the silicon-bearing gas is disilane (Si_2H_6).

32. A tungsten silicon nitride ($W_xSi_yN_z$) film on a surface of a substrate, formed by:

30 (a) placing the substrate in a reactor chamber;

- 25 -

- (b) heating the substrate;
- (c) flowing tungsten hexafluoride (WF_6), nitrogen trifluoride (NF_3), hydrogen, and a silicon-bearing gas into the reactor chamber and over the surface of the heated substrate; and
- 5 (d) striking a plasma over the substrate.

33. The film of claim 32 wherein the silicon-bearing gas is silane (SiH_4).

10 34. The film of claim 32 wherein the silicon-bearing gas is disilane (Si_2H_6).

35. The film of claim 32 further comprising injecting an inert gas into the chamber.

15 36. A method for forming a titanium silicon nitride ($Ti_xSi_yN_z$) film on a surface of a substrate, comprising steps of:

- (a) placing the substrate in a reactor chamber;
- (b) heating the substrate; and
- 20 (c) flowing titanium tetrachloride ($TiCl_4$), nitrogen trifluoride (NF_3), a silicon-bearing gas, and hydrogen into the reactor chamber and over the surface of the heated substrate.

37. The method of claim 36 wherein the silicon-bearing gas is silane (SiH_4).

25 38. The method of claim 36 wherein the silicon-bearing gas is disilane (Si_2H_6).

- 26 -

39. The method of claim 36 wherein the substrate is a silicon wafer having integrated circuit (IC) structures formed thereon.

40. The method of claim 36 wherein the step of placing the substrate in
5 a reactor chamber comprises moving the substrate from a vacuum load lock chamber into the reactor chamber.

41. The method of claim 36 wherein the reactor chamber is a single-wafer CVD reactor chamber adapted to a cluster tool material handling
10 system.

42. The method of claim 36 wherein the reactor chamber is a batch reactor chamber, and in the placing the substrate step, a batch of more than one wafer is moved into the CVD reactor chamber from a vacuum
15 load lock chamber.

43. A method for forming a titanium silicon nitride ($Ti_xSi_yN_z$) film on a surface of a substrate, comprising steps of:

(a) placing the substrate in a reactor chamber;
20 (b) heating the substrate;
(c) flowing titanium tetrachloride ($TiCl_4$), nitrogen trifluoride (NF_3), a silicon-bearing gas, and hydrogen into the reactor chamber; and
(d) striking a plasma over the substrate.

25 44. The method of claim 43 wherein the silicon-bearing gas is silane (SiH_4).

45. The method of claim 43 wherein the silicon -bearing gas is disilane (Si_2H_6).

- 27 -

46. The method of claim 43 further comprising injecting an inert gas into the chamber.

47. The method of claim 43 wherein the substrate is a silicon wafer
5 having integrated circuit (IC) structures formed thereon.

48. The method of claim 43 wherein the step of placing the substrate in a reactor chamber comprises moving the substrate from a vacuum load lock chamber into the reactor chamber.

10

49. The method of claim 43 wherein the reactor chamber is a single-wafer CVD reactor chamber adapted to a cluster tool material handling system.

15

50. The method of claim 43 wherein the reactor chamber is a batch reactor chamber, and in the placing the substrate step, a batch of more than one wafer is moved into the CVD reactor chamber from a vacuum load lock chamber.

20

51. A titanium silicon nitride ($Ti_xSi_yN_z$) film on a surface of a substrate, formed by:

- (a) placing the substrate in a reactor chamber;
- (b) heating the substrate; and
- (c) flowing tungsten hexafluoride (WF_6), nitrogen trifluoride

25

(NF_3) , hydrogen, and a silicon-bearing gas into the reactor chamber and over the surface of the heated substrate.

52. The film of claim 51, wherein the silicon-bearing gas is silane (SiH_4).

30

53. The film of claim 51 wherein the silicon-bearing gas is disilane (Si_2H_6).

54. A titanium silicon nitride ($\text{Ti}_x\text{Si}_y\text{N}_z$) film on a surface of a substrate,
5 formed by:
(a) placing the substrate in a reactor chamber;
(b) heating the substrate;
(c) flowing tungsten hexafluoride (WF_6), nitrogen trifluoride
(NF_3), a silicon-bearing gas, and hydrogen into the reactor chamber and
10 over the surface of the heated substrate; and
(d) striking a plasma over the substrate.

55. The film of claim 54 wherein the silicon-bearing gas is silane
(SiH_4).

15 56. The film of claim 54 wherein the silicon-bearing gas is disilane
(Si_2H_6).

57. The film of claim 54 further comprising injecting an inert gas into
20 the chamber.

58. A method for forming a nitrided film of a transitional metal on a
surface of a substrate, comprising steps of:
(a) placing the substrate in a reactor chamber;
25 (b) heating the substrate; and
(c) flowing a gas bearing the transitional metal, nitrogen
trifluoride (NF_3), and hydrogen (H_2) into the reactor chamber and over
the surface of the heated substrate.

- 29 -

59. The method of claim 58 wherein the gas bearing a transitional metal
is tungsten hexafluoride (WF_6).

60. The method of claim 58 wherein the gas bearing a transitional metal
5 is titanium tetrachloride ($TiCl_4$).

61. A composite metal film on a surface of a substrate, the film
comprising a transitional metal and a nitride of the transitional metal,
formed by:

10 (a) placing the substrate in a reactor chamber;
(b) heating the substrate; and
(c) flowing a gas bearing the transitional metal, nitrogen
trifluoride (NF_3), and hydrogen (H_2) into the reactor chamber and over
the surface of the heated substrate.

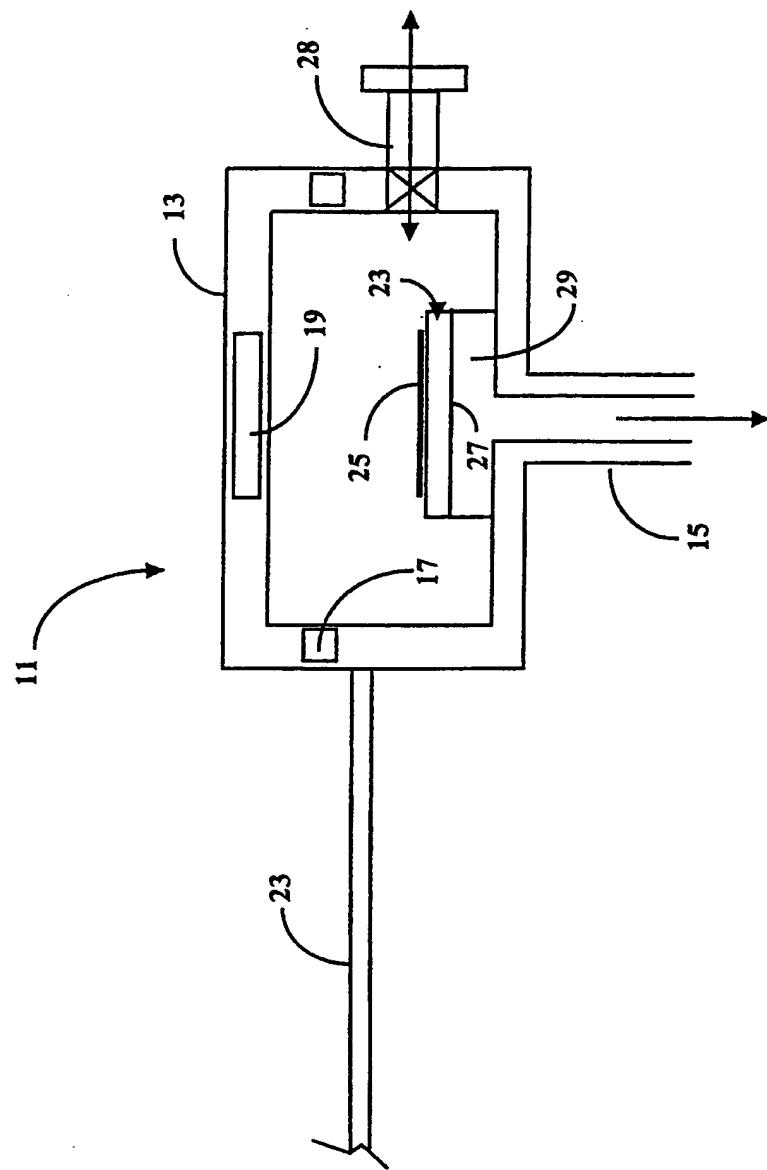


Fig. 1

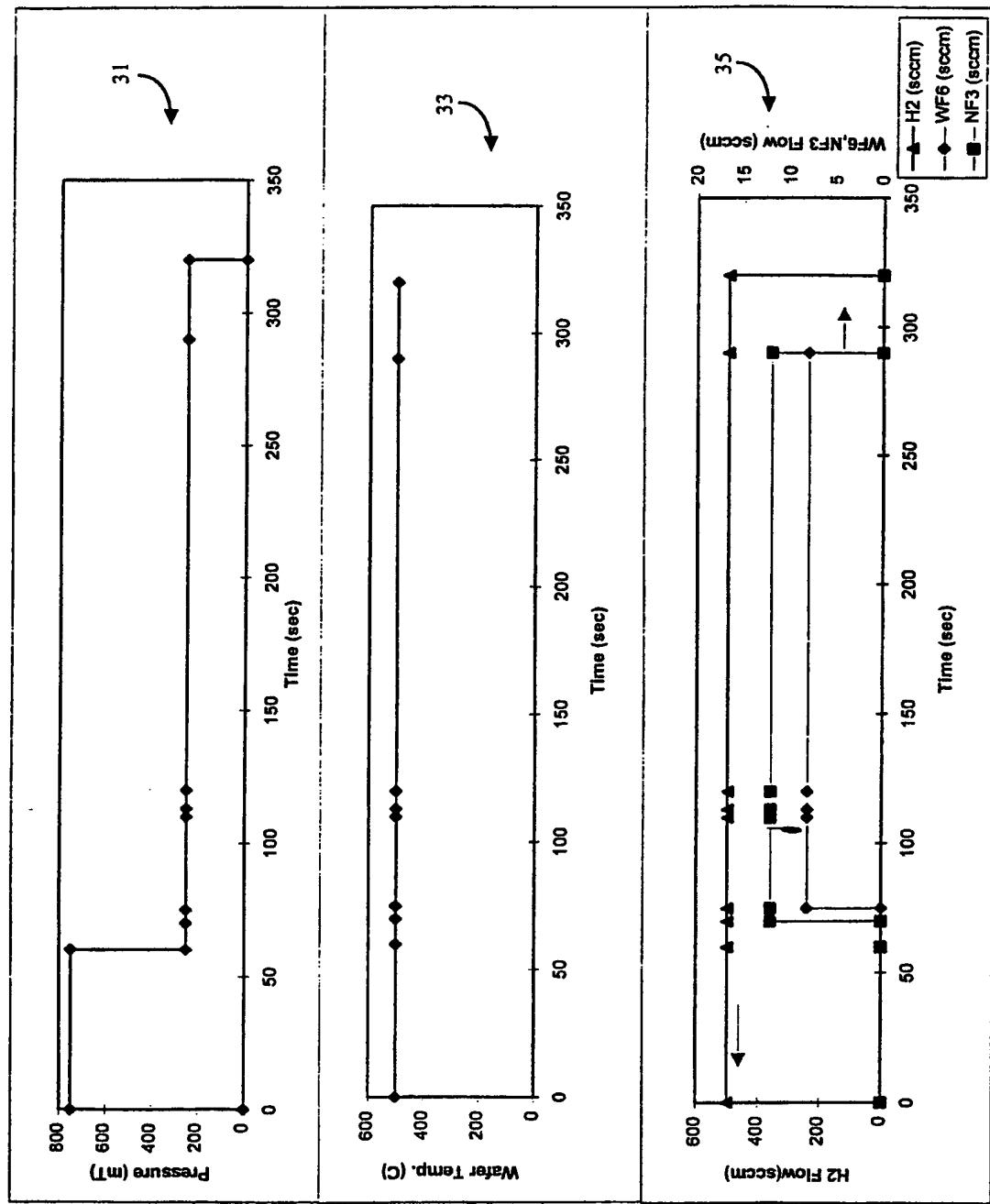


Fig. 2

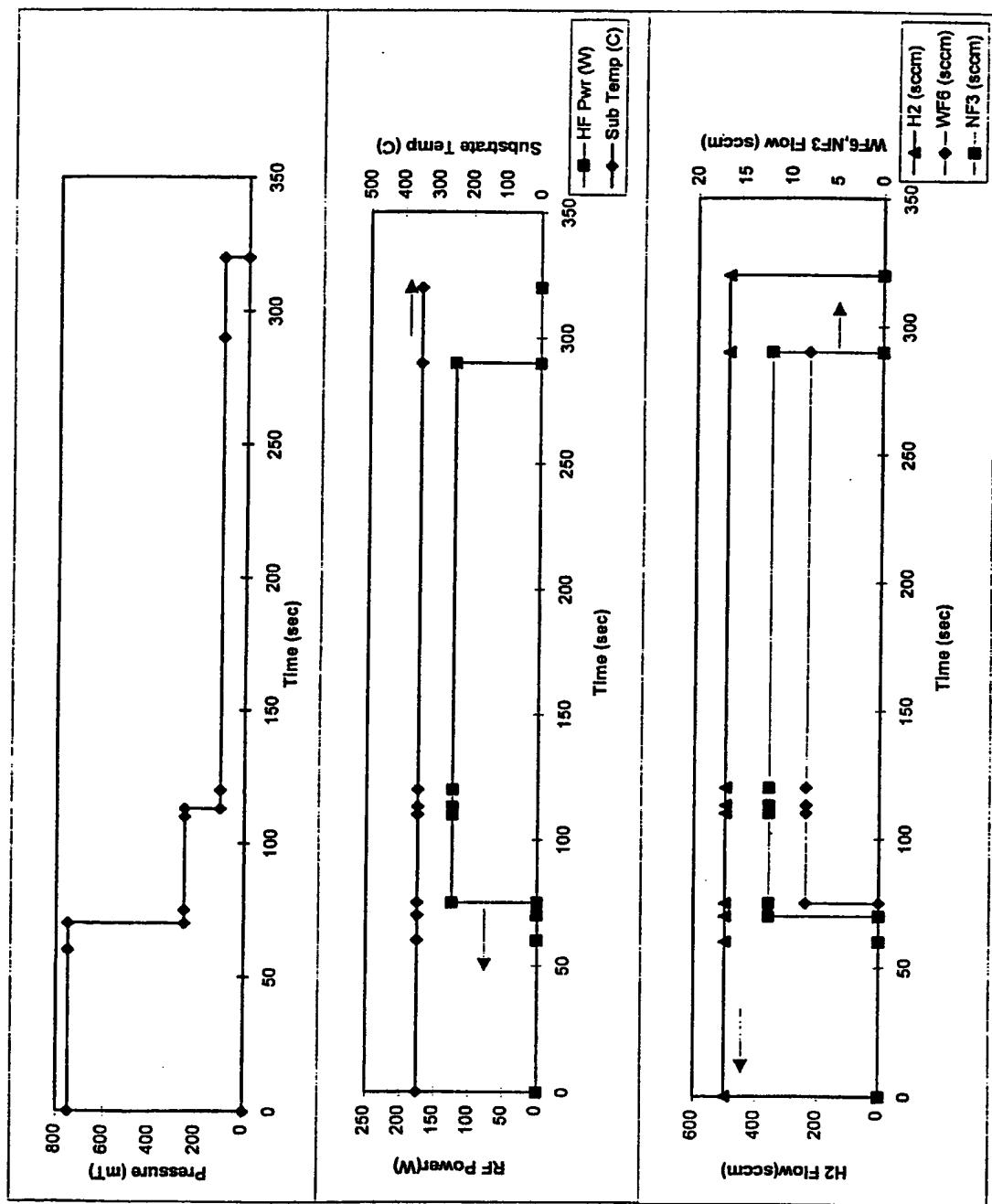


Fig. 3

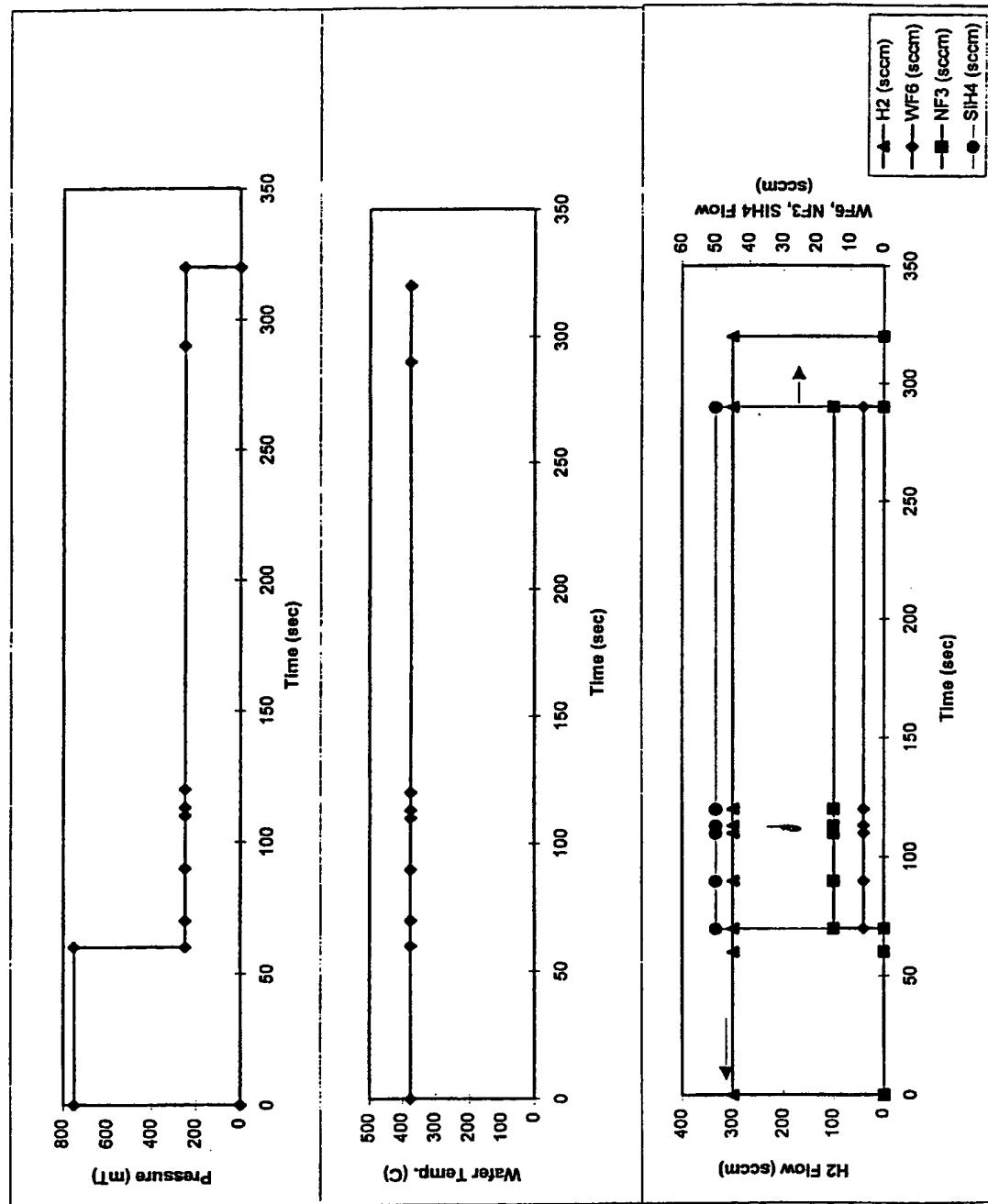


Fig. 4

5/8

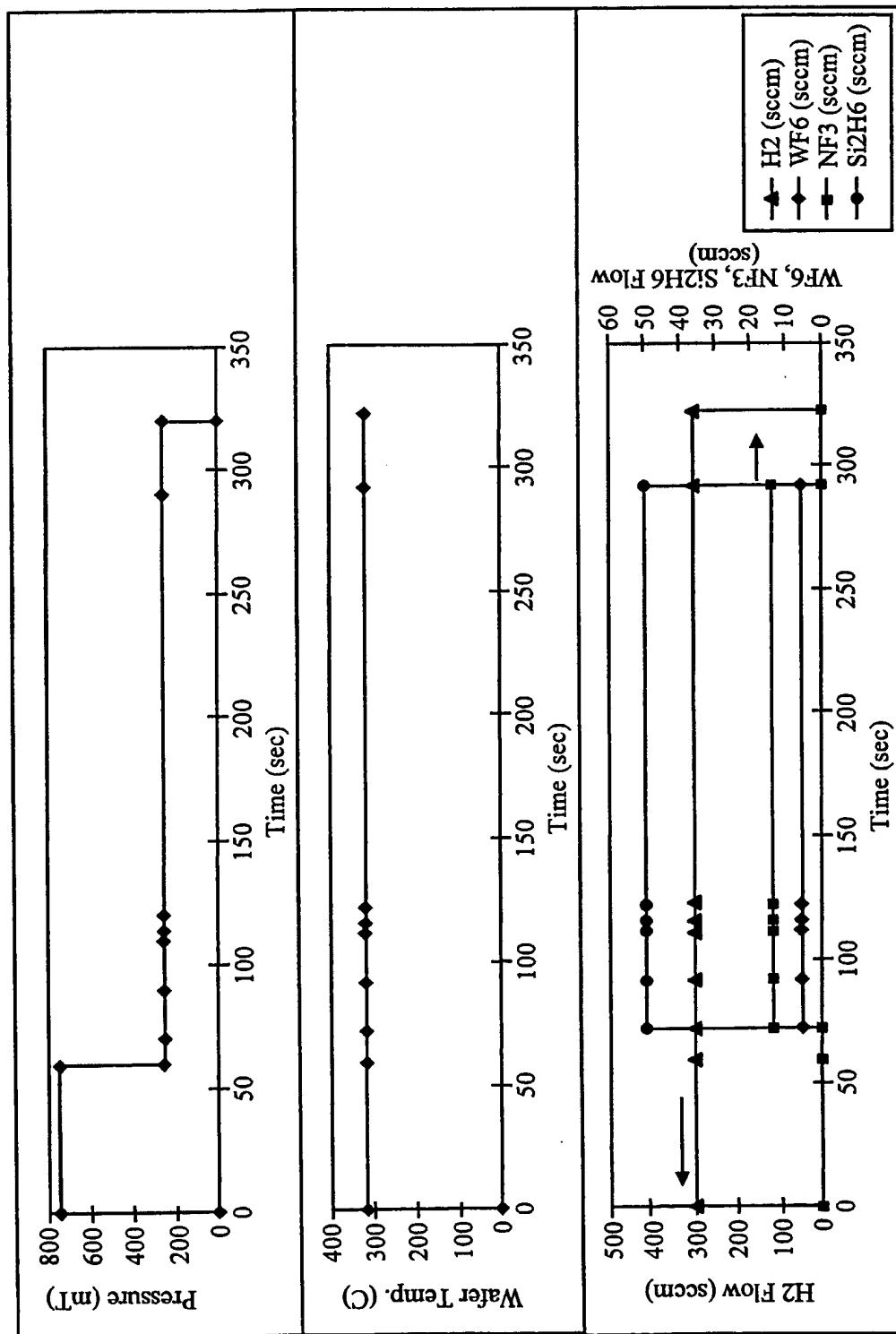


Fig 5

6/8

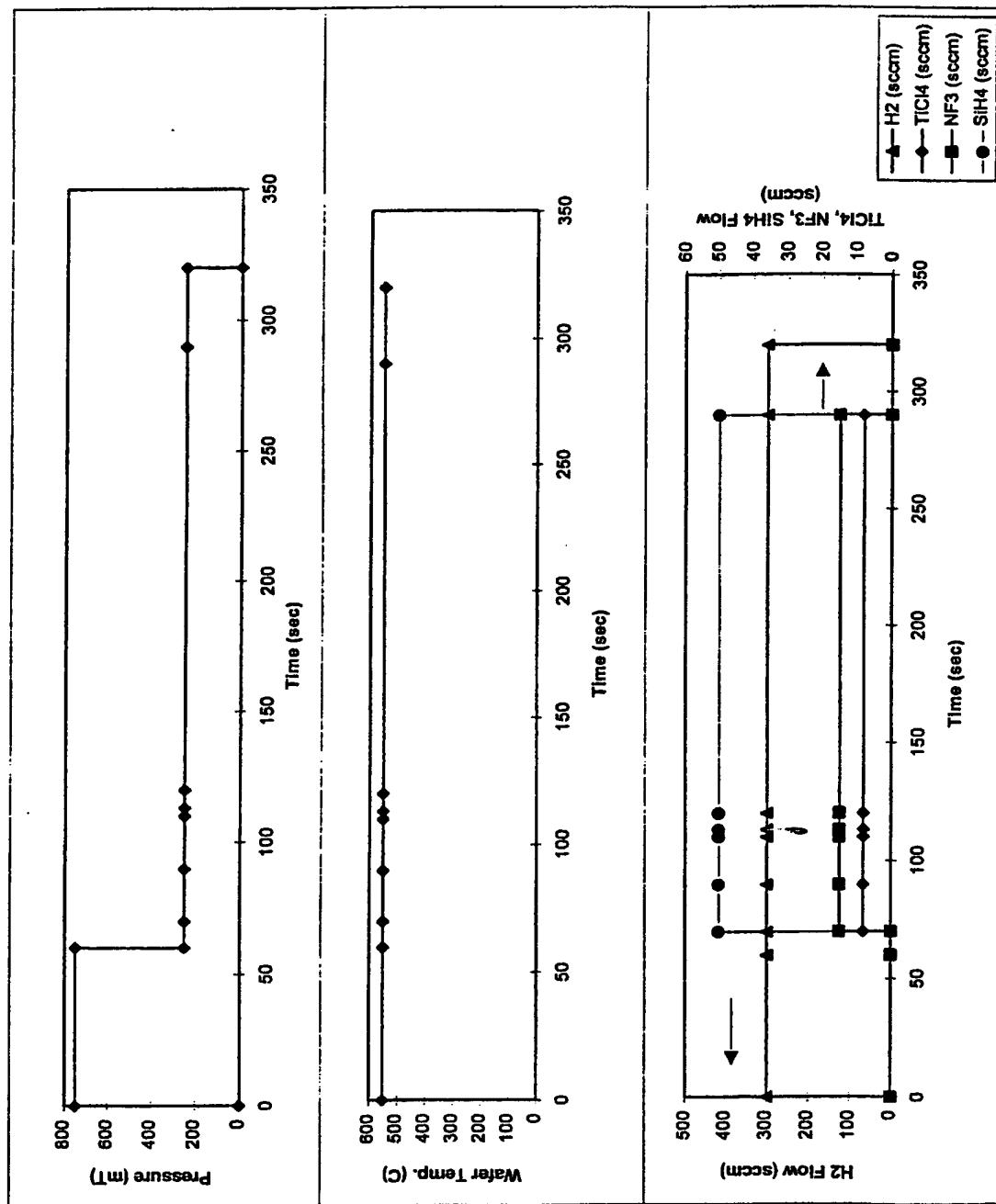


Fig. 6

7/8

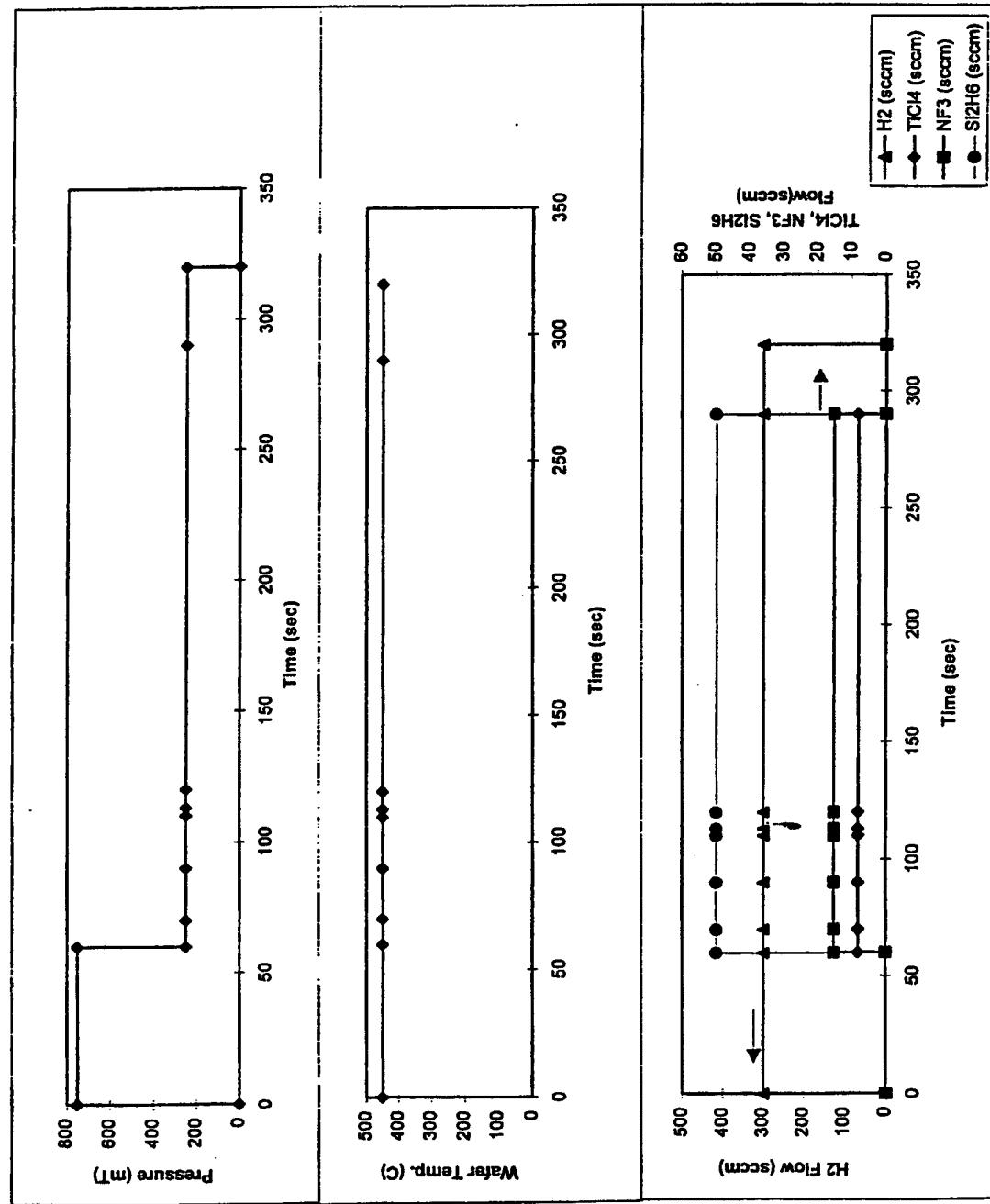


Fig. 7

8/8

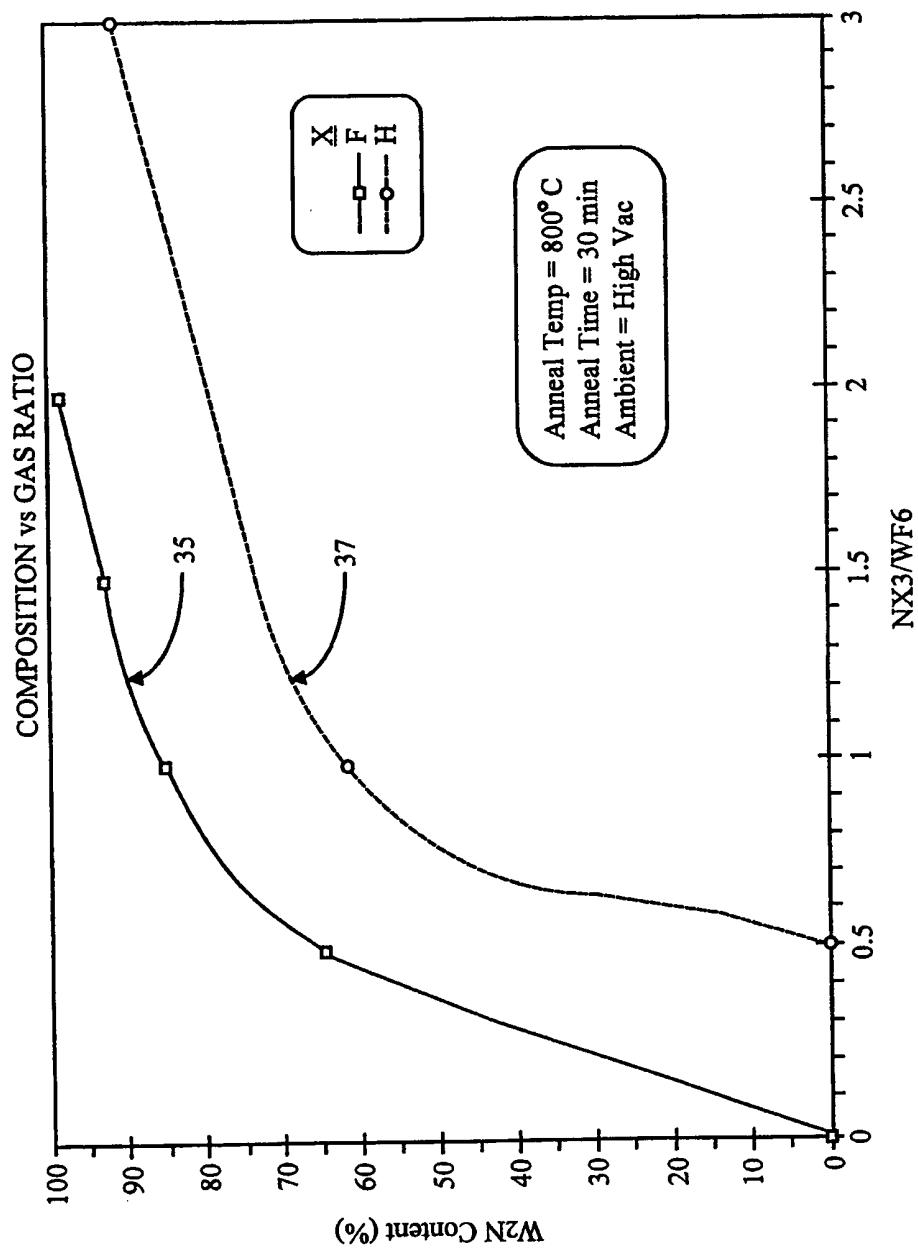


Fig. 8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/21449

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B05D 5/12; C23C 16/34; H05H 1/24; B32B 18/00; G11B 5/66

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 427/126.1, 248.1, 255, 255.1, 576; 118/719, 723R, 723MW, 723 E; 428/628, 689, 694NP

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS search terms - chemical vapor deposition, nitrogen fluoride, tungsten nitride, titanium nitride

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,114,750 A (HOWARD) 19 May 1992, col.1 lines 1-19	1-5, 14-20, 36-42, 58-60
Y	US 4,897,709 A (YOKOYAMA et al.) 30 January 1990, col.1 lines 7-18	1-5, 14-20, 36-42, 58-60
A	US 5,429,991 A (IWASAKI et al.) 04 July 1995, col.3 lines 4-59	6-13,21-35, 43-57, 61
A	US 4,830,891 A (NISHITANI et al.) 16 May 1989, col.3 line 40 - col.4 line 8	6-13,21-35,43-57,61

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents:	*T*	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"B" earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z*	document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

26 JANUARY 1998

Date of mailing of the international search report

04 MAR 1998

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Authorized officer
Bret Chen
[Signature]

Facsimile No. (703) 305-3230

Telephone No. (703) 308-0661

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/21449

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

427/126.1, 248.1, 255, 255.1, 576; 118/719, 723R, 723MW, 723 E; 428/628, 689, 694NF